EXAM Fonctions et Réactions Organiques III / CH-234 June 27, 2019

Duration of the exam: 120 Minutes

Answer the Questions only on the associated sheet of the question!

NO loose sheets are accepted!

NO PENCIL or RED pen is allowed!

Allowed aids: NONE

Name:		
First Name:		
Stud. ID No.		
Place Number		
Signature		
Exercise 1	10 Points	
Exercise 2	10 Points	
Exercise 3	10 Points	
Exercise 4	10 Points	
Exercise 5	10 Points	
Exercise 6	10 Points	
Exercise 7	10 Points	
Exercise 8	10 Points	
Exercise 9	10 Points	
Exercise 10	10 Points	
Total Points	100 Points	
GRADE		

GOOD LUCK!

1. Characterize the properties of the substituents by ticking the appropriate answers! (10P)

CAUTION: Wrong answers lead to a deduction of points. There is a minimum of 0 points for each subpart of the question. (2P max. for each subpart)

		σ -donor	σ-acceptor	π -donor	π -acceptor
a)	Me Me N He	☐ yes ☐ no	☐ yes ☐ no	☐ yes ☐ no	☐ yes ☐ no
b)	CF ₃	☐ yes ☐ no	□ yes □ no	□ yes □ no	☐ yes ☐ no
c)	CI	☐ yes ☐ no	□ yes □ no	☐ yes ☐ no	☐ yes ☐ no
d)	OMe	□ yes □ no	□ yes □ no	□ yes □ no	□ yes □ no
e)	NO ₂	□ yes	☐ yes ☐ no	☐ yes ☐ no	☐ yes

2a.	Characterize	the following	molecules	according	to	Hückel	criteria	by	ticking	the
app	ropriate answ	er! (5P)								

		aromatic	anti-aromatic	non-aromatic	
a)					
b)					
c)	Ф				
d)					
e)					

2b. Name the asked molecule according to the Hantzsch-Widman system (2P)

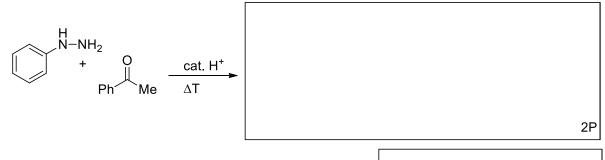
a) ON	b) S
Name:	Name:

2c. Competing Reactants: An **equimolar** (1:1) mixture of two starting materials is reacted with just **1 equivalent** of the indicated reagent. **Encircle** the major product that is formed. (3P)

a)
$$V_{NO_2}$$
 V_{NMe_2} V_{NO_2} V_{NO_2} V_{NMe_2} V_{NO_2} V_{NMe_2} V_{NO_2} V_{NO_2} V_{NMe_2} V_{NO_2} V_{NO_2} V_{NMe_2} V_{NO_2} V_{NO_2

3a. Aniline is chlorinated by an electrophilic aromatic substitution reaction. D reasonable mesomeric structures of the σ -complex intermediate for the chlorination path. (3P)	
3b. The <i>Hammett</i> -Equation provides reaction mechanism insights. The showr were measured for this substitution reaction. (3P)	ı values
Nu Hammett equation	σ_{p}
$\frac{\log \frac{1}{\kappa_{H}} = \rho \sigma}{\log \frac{1}{\kappa_{H}} = \rho \sigma} - Me^{-\kappa_{H}}$	0.36 0.12 -0.4 0.21
These results indicate that the reaction proceeds <i>faster</i> with substrates <i>donating substituents</i> . Please answer the following questions:	having
 a) What partial charge has the transition state: □ positive □ neutral □ negative 	
b) What sign has then the value "ρ" in the equation?:□ plus □ minus	
c) With which of the three given substituents R, the reaction proceeds fastest? $R = \Box CN \qquad \Box NMe_2 \Box Et$,
3c. The "unassigned/uncolored" frontier orbitals for a model Diels-Alder reashown. Color the correct orbital lobes that are involved in the Diels-Alder procename/characterize them. (4P)	
Tick:	
1P 2P	1P

4. Complete the following scheme by adding the missing structures as well as the reaction names when requested. (10P)



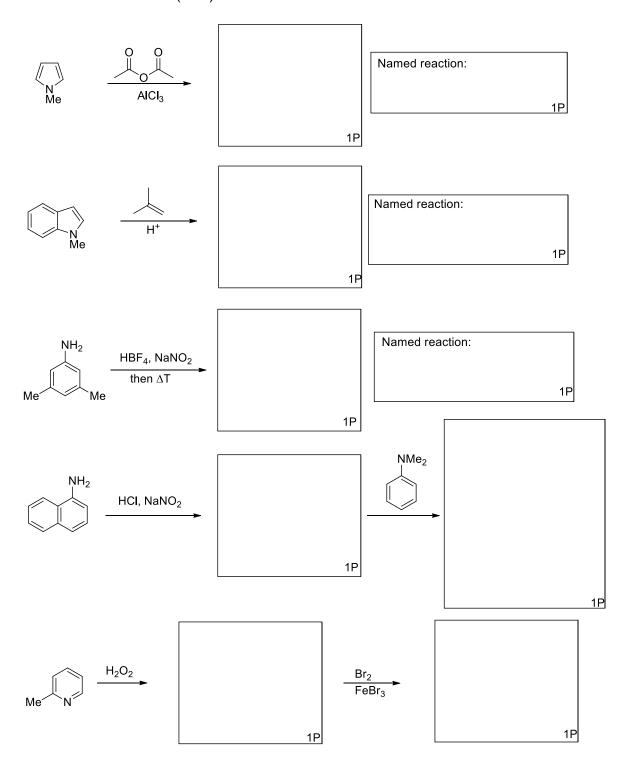
Reaction Name 1P

1P

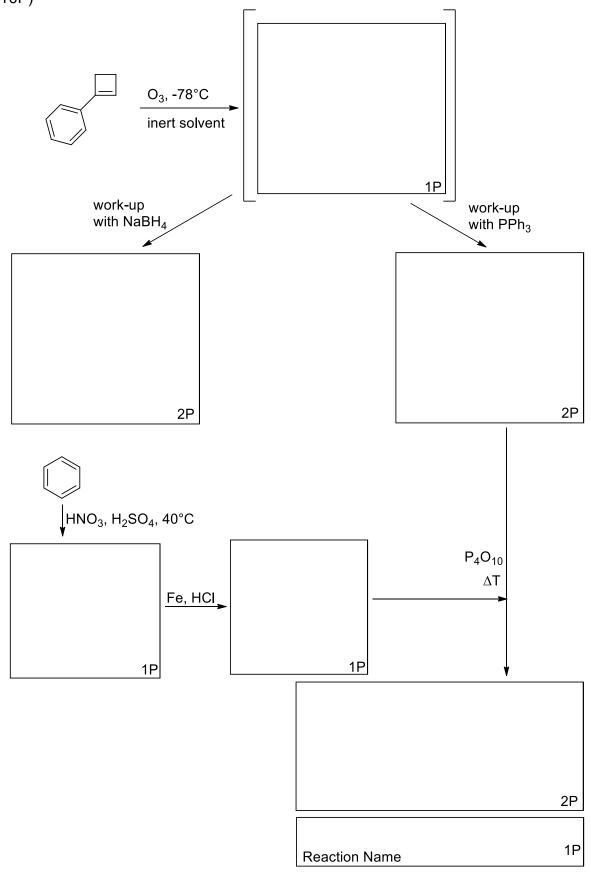
Reaction Name

 $Ph \stackrel{O}{\longrightarrow} Ph \qquad \frac{1) P_4 S_{10}}{2) H_3 PO_4, dehydrating}$

5. Complete the following schemes by adding the major product! If asked, give the name of the reaction. (10P)



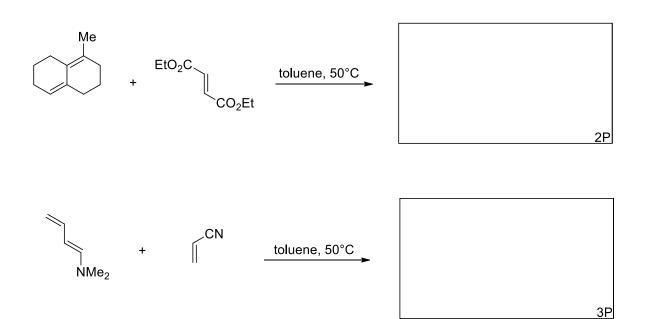
6. Complete the blanks by filling in the missing compounds and the reaction name. (10P)

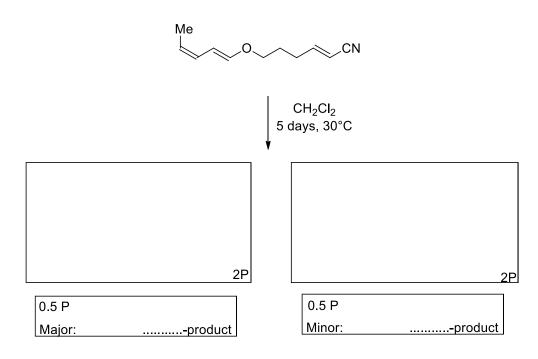


7a. 1,4-Dimethoxy benzene is submitted to a Vilsmeyer-Haack formylation. Draw the required reagents and the product. Provide the appropriate details on the reaction mechanism by drawing the active reagent and relevant intermediates (4P).

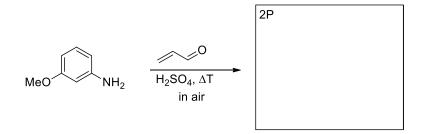
7b. The Hantzsch synthesis gives access to the shown dihydropyridine. Draw the required starting materials and illustrate the reaction mechanism in appropriate detail by drawing the relevant intermediates and condensation steps! (6P)

8. Fill in the blanks! Pay especially attention to the **regio**- and **stereochemistry** of your products. **Clearly** mark the stereochemistry in your answers. (10P)





9. Draw the main product of the shown reactions and provide their reaction name. (10P)



10. 1) Do the starting materials react with each other under the given conditions?
2) Are the shown products the expected main products?

If not: draw the correct product in the box or explain in very FEW words why no reaction takes place (10P total)
Fill out only when one NO before:

Give a reason why there is no reaction

HO H ₂	SO ₄	НО	Me
Reaction?	☐ yes	□no	·
if yes, correct main product	?	□no	

i iii out only when one ito before.
Give a reason why there is no reaction
or draw the correct reaction product
·

Ph N₃
CuSO₄,
Na ascorbate

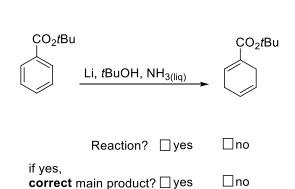
Reaction? □yes □no

if yes,
correct main product? □yes □no

Fill out only when one NO before:
Give a reason why there is no reaction
or draw the correct reaction product

F	Bu _{`S} ⊝	→	SBu
	Reaction?	□yes	□no
if yes, correct r	nain product?	⊇	□no

Fill out only when one NO before: Give a reason why there is no reaction



or draw the correct reaction product	
Fill out only when one NO before:	

Give a reason why there is no reaction or draw the correct reaction product